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(54) Title: **POLYESTER DISPERSANTS**

(57) Abstract: A dispersant which comprises a polyamine (e.g. polyallylamine) or polyimine (e.g. polyethyleneimine) backbone chain containing side chains of two or more different types of polyester chain wherein at least one type of polyester chain is derivable from one or more hydroxy carboxylic acids all of which contain a C₁₋₆-alkylene group or lactone thereof such as ε-caprolactone and/or δ-valerolactone and at least one other type of polyester chain derivable from one or more hydroxy carboxylic acids wherein at least one of the hydroxy carboxylic acids contains a C₈₋₃₀-alkylene chain (e.g. 12-hydroxystearic acid) or a C₈₋₃₀-alkenylene chain (e.g. ricinoleic acid) or lactone thereof.

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POLYESTER DISPERSANTS

The present invention relates to polyester dispersants comprising a polyamine or polyimine chain containing two or more different types of polyester chain attached to the polyamine or polyimine chains.

WO 94/21368 discloses a dispersant comprising a polyethyleneimine residue
5 carrying a plurality of poly(carbonylalkyleneoxy) chains each chain containing a plurality of repeat units derivable from 6-hydroxyhexanoic acid and at least one other hydroxycarboxylic acid selected from ricinoleic acid, 12-hydroxystearic acid, 12-hydroxydodecanoic acid, 5-hydroxydodecanoic acid, 5-hydroxydecanoic acid and 4-hydroxydecanoic acid. These dispersants were shown to be particularly effective when
10 dispersing pigments in non-polar solvents such as xylene.

WO 98/19784 discloses a dispersant which contains a polyester chain derived from optionally alkyl substituted ϵ -caprolactone and δ -valerolactone attached via amide or salt groups to a polyamine or polyimine backbone chain such as polyallylamine or polyalkyleneimine, for example polyethyleneimine. These dispersants are particularly
15 effective for dispersing pigments in polar organic liquids such as butanol and methoxy propylacetate.

EP 713 894 discloses dispersants which contain a polyester chain which is attached to a polyamine or polyimine backbone chain via a Michaels addition reaction. The polyester chain contains oxy-C₃₋₁₀-alkylene carbonyl groups. These dispersants are
20 effective for dispersing pigments in non-polar liquids such as xylenes and in polar organic liquids such as alcohols and ketones.

None of these prior art documents disclose or envisage dispersants wherein the polyamine or polyimine backbone chain contains different types of polyester side chains. It has now been found that such dispersants exhibit improved dispersion characteristics in
25 both polar and non-polar organic liquids without significant deterioration of dispersion characteristics in the one type of organic liquid.

According to the invention there is provided a dispersant which comprises a polyamine or polyimine backbone chain containing side chains of two or more different types of polyesters chain wherein at least one type of polyester chain is derivable from
30 one or more hydroxy carboxylic acids all of which contain a C₁₋₆-alkylene group or lactone thereof and at least one other type of polyester chain derivable from one or more hydroxy carboxylic acids wherein at least one of the hydroxy carboxylic acids contains a C₈₋₃₀-alkylene or C₈₋₃₀-alkenylene group or lactone thereof, including salts of such dispersants. This is referred to hereinafter as The Dispersant.

35 Preferably the total amount of polyester chains attached to the polyamine or polyimine backbone is from 3:1 to 20:1 more preferably from 5:1 to 20:1, even more

preferably from 10:1 to 15:1 and especially from 8:1 to 15:1 by weight of the polyamine or polyimine.

The polyester chain which is derivable from hydroxy carboxylic acids or lactones thereof all of which contain a C₁₋₆-alkylene group is a poly(oxy C₁₋₆-alkylene carbonyl) chain (hereinafter POAC 1). It may be linear or branched. The POAC 1 chain may be derivable from a single hydroxy carboxylic acid or lactone thereof or from different hydroxy carboxylic acids or lactones thereof.

Preferably, POAC 1 is derivable from hydroxy carboxylic acids or lactones thereof all of which contain a C₂₋₆-alkylene group.

Examples of hydroxy carboxylic acids from which POAC 1 may be derived are glycolic acid, 6-hydroxy hexanoic acid and 5-hydroxy pentanoic acid. Examples of suitable lactones are optionally alkyl substituted ϵ -caprolactone, optionally alkyl substituted δ -valerolactone and β -propiolactone.

When the polyester chain of POAC 1 is branched it may be conveniently derived from alkyl substituted ϵ -caprolactones. These may be made by oxidation of alkyl substituted cyclohexanone as described in WO 98/19784. Many of these alkyl substituted ϵ -caprolactones are available as mixtures. The alkyl substituent is preferably C₁₋₆-alkyl and especially C₁₋₄-alkyl which may be linear or branched. Examples of alkyl substituted ϵ -caprolactone are 7-methyl, 3-methyl, 5-methyl, 6-methyl, 4-methyl, 5-tert butyl, 4,6,6-trimethyl and 4,4,6-trimethyl substituted ϵ -caprolactone. An example of an alkyl substituted δ -valerolactone is β -methyl- δ -valerolactone.

When POAC 1 is derivable from a single hydroxy carboxylic acid or lactone thereof it is preferably an alkyl substituted ϵ -caprolactone and especially ϵ -caprolactone itself.

However, it is preferred that POAC 1 is derivable from 2 or more different hydroxy carboxylic acids or lactones thereof and especially from two different hydroxy carboxylic acids or lactones thereof. When POAC 1 is derivable from two different lactones, the lactones are preferably optionally alkyl substituted ϵ -caprolactone and δ -valerolactone and especially ϵ -caprolactone and δ -valerolactone. When POAC 1 is derivable from glycolic acid and one or more lactones, the lactone is preferably ϵ -caprolactone.

The polyester chain which is derivable from one or more hydroxy carboxylic acids at least one of which contains a C₈₋₃₀-alkylene or C₈₋₃₀-alkenylene group, or lactone thereof, is hereinafter referred to as POAC 2. It may be linear or branched and preferably the alkylene or alkenylene group contains not greater than 24 and especially not greater than 20 carbon atoms. It is also preferred that the alkylene or alkenylene group contains not less than 10, more preferably not less than 12 and especially not less than 16 carbon atoms. Examples of suitable hydroxy carboxylic acids from which POAC 2 is derivable are ricinoleic acid, 12-hydroxy stearic acid, 12-hydroxy dodecanoic acid, 5-hydroxy dodecanoic acid, 5-hydroxy decanoic acid and 4-hydroxy decanoic acid.

In one preferred aspect of the invention, POAC 2 is derivable from a single hydroxy carboxylic acid which contains a C₈₋₃₀-alkylene or C₈₋₃₀-alkenylene group such as 12-hydroxy stearic acid or ricinoleic acid.

5 In another preferred aspect of the invention, POAC 2 is derivable from two or more hydroxy carboxylic acids one of which contains a C₈₋₃₀-alkylene or C₈₋₃₀-alkenylene group and at least one hydroxy carboxylic acid which contains a C₁₋₆-alkylene group, preferably a C₂₋₆-alkylene group, or lactone thereof. Examples of POAC 2 derivable from two different kinds of hydroxy carboxylic acids or lactones thereof are those derivable from ricinoleic acid and optionally alkyl substituted ϵ -caprolactone and those derivable from ricinoleic acid, optionally alkyl substituted ϵ -caprolactone and δ -valerolactone. When POAC 2 is derivable from optionally alkyl substituted ϵ -caprolactone, the lactone is preferably unsubstituted.

In a particularly preferred class of dispersant, the dispersant contains only two different types of polyester chain, i.e. POAC 1 and POAC 2.

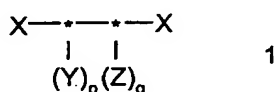
15 The polyester chains POAC 1 and POAC 2 may be attached to the polyamine or polyimine backbone chains via amide and/or salt linkages or they may be attached via a linkage which contains an ethylenically unsaturated group. In all these methods of attachment, the polyamine is preferably polyallylamine or polyvinylamine and the polyimine is preferably poly (C₂₋₆-alkyleneimine) and especially polyethyleneimine. The polyimines may be linear but are preferably branched. Linear polyethyleneimines can be prepared by hydrolysis of poly (N-acyl) alkyleneimines as described, for example, by Takeo Saegusa et al in Macromolecules, 1972, Vol. 5, page 4470. The branched polyethyleneimines of differing molecular weights are commercially available from BASF and Nihon Shokubai. Polyallylamine and poly (N-alkyl) allylamines of differing molecular weights are commercially available from Nitto Boseki. Polyvinylamine of differing molecular weights are available from Mitsubishi Kasei. Poly (propyleneimine) dendrimers are commercially available from DSM Fine Chemicals and poly (amidoamine) dendrimers are available as "Starburst" dendrimers from Aldrich Chemical Co.

30 In the case where the polyester chains are attached via a linkage containing an ethylenically unsaturated group, the polyamine may also be a diamine which may be aliphatic or aromatic. Examples of suitable diamines are ethylenediamine, N,N'-dimethyl ethylenediamine, piperazine, 2-methyl piperazine, 2,5-dimethyl piperazine, 2,3-dimethyl piperazine, 1,4-bis(3-aminopropyl)piperazine, N-(2-aminoethyl)piperazine, isophoronediamine, polyoxy propylenediamine, polyoxy ethylenediamine, bis(4-amino-3-methyl dicyclohexyl)methane, diamino dicyclohexyl methane, bis(aminomethyl)cyclohexane, m-xylylenediamine, α -(m-aminomethyl)ethylamine, α -(p-aminophenyl)ethylamine, m-phenylenediamine, diaminodiphenyl methane, diaminodiphenyl sulphone and norbornanediamine.

When the polyester chains are attached via a linkage which contains an ethylenically unsaturated group the polyamine or polyimine is preferably polyallylamine, polyvinylamine or poly(C₂₋₆-alkyleneimine) and especially polyethyleneimine.

The number average molecular weight of the polyamine or polyimine is preferably from 500 to 600,000, more preferably from 1,000 to 200,000, even more preferably from 1,000 to 100,000 and especially from 5,000 to 100,000.

When the dispersant contains only two different types of polyester chain it may be conveniently represented by general formula 1



wherein

X—---X represents the polyamine or polyimine backbone polymer;

Y represents a polyester chain residue POAC 1;

Z represents a polyester chain residue POAC 2;

p and q are integers; and

(p + q) is from 2 to 2000.

Preferably, (p + q) is not less than 4 and especially not less than 10. It is also preferred that (p + q) is not greater than 1000 and especially not greater than 500. The ratio of p:q may vary from 10:1 to 1:10 and preferably from 5:1 to 1:5 by molar ratio. It is, however, preferred that the molar ratio of p:q is from 1:1 to 5:1, i.e. the dispersant contains a greater molar amount of the polyester chain derivable from hydroxycarboxylic acids wherein all the hydroxycarboxylic acids contain an optionally alkyl substituted C₂₋₆-alkylene group, or lactones thereof. Particularly useful dispersant have been obtained when the molar ratio of p:q is 4:1.

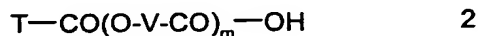
When the POAC 1 and POAC 2 residues are linked to the polyamine or polyimine backbone via amide and/or salt linkages, the dispersant may be made by either reacting the polyamine or polyimine with the appropriate hydroxycarboxylic acids or lactones thereof in a stepwise manner or preferably by reacting the polyamine or polyimine with preformed polyesters containing the polyester chain.

When the former, less preferred, method is used the polyamine or polyimine acts as a polymerisation terminating group and the different polyester chains are built sequentially. When the first polyester chain has been built on the polyamine or polyimine backbone the resultant terminal hydroxy group need not be reacted with a polymerisation terminating group in order to prevent the hydroxycarboxylic acids or lactones required for building the second polyester chain from adding to the first polyester chain. However, it is preferred to prepare the precursors containing POAC 1 and POAC 2 chains separately

and to subsequently react these precursors with the polyamine or polyimine. The preformed polyester chains, POAC 1 and POAC 2 may be reacted with the polyimine or polyamine either sequentially or, preferably, simultaneously.

It is, of course, possible to use a combination of such methods of preparation wherein one of the polyester chains is built on to the polyamine or polyimine backbone polymer by reacting with the appropriate hydroxycarboxylic acids or lactones thereof and optionally after reacting the terminal hydroxy group of this first polyester chain with a polymerisation terminating compound the polyamine or polyimine containing the first polyester chain is reacted with the second preformed polyester.

As noted hereinbefore, it is preferred to prepare the dispersant by preforming the polyester chains. The preparation of the polyester precursors is most conveniently achieved by reacting the appropriate hydroxycarboxylic acids with a polymerisation terminating compound to give a poly(oxyalkylene carbonyl) chain containing a polymerisation terminating group and/or poly(oxyalkenylene carbonyl) chain containing the polymerisation terminating group. The polymerisation terminating compound is preferably a carboxylic acid T-COOH which may be aromatic, alicyclic, heterocyclic or preferably aliphatic. The polyester precursor thereby carries a terminal carboxylic acid and may be represented by formula 2



wherein

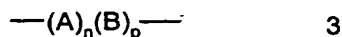
T is an aromatic, alicyclic, heterocyclic or aliphatic residue all of which may be substituted;

V is the alkylene or alkenylene group of the appropriate polyester chain; and
m is from 2 to 100.

The polyester acid of formula 2 is hereinafter referred to as a TPOAC acid.

Preferably m is not greater than 70, more preferably not greater than 50 and especially not greater than 20.

When (O-V-CO)_m represents POAC 1 obtainable from two different hydroxycarboxylic acids or lactones thereof, the residue of POAC 1 chain may be conveniently represented by formula 3 in a preferred embodiment of POAC 1



wherein

A represents an oxyalkylene carbonyl chain derivable from optionally alkyl substituted ϵ -caprolactone;

B represents an oxyalkylene carbonyl chain derivable from δ -valerolactone;

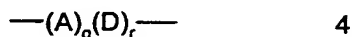
n and p are integers; and

n + p is from 2 to 100.

Preferably (n + p) is not greater than 70, more preferably not greater than 50 and especially not greater than 20.

The ratio of n:p is preferably between 12:1 and 1:6, more preferably between 8:1 and 1:2 and especially between 6:1 and 1:2.

5 When (O-V-CO)_m represents POAC 2 which is derivable from two different types of hydroxycarboxylic acids or lactones thereof, the residue of POAC2 chain may be conveniently represented by formula 4 in a preferred embodiment of POAC 2



10 wherein

A represents an oxyalkylene carbonyl chain derivable from optionally alkyl substituted 6-hydroxyhexanoic acid or ϵ -caprolactone;

D represents an oxy (C₈₋₃₀)-alkylene carbonyl chain and/or an oxy (C₈₋₃₀)-alkenylene carbonyl chain;

15 q and r are integers; and

q + r is from 2 to 100.

Preferably (q + r) is not greater than 70, more preferably not greater than 50 and especially not greater than 20.

20 The ratio of q:r is preferably between 4:1 and 1:4 and especially between 2:1 and 1:2.

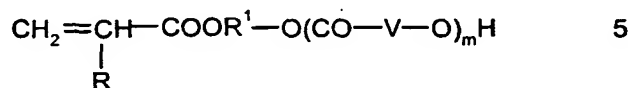
The polymerisation terminating acid T-COOH is preferably free from amino groups and is preferably a C₁₋₂₅-aliphatic carboxylic acid which may be linear or branched and is optionally substituted by hydroxy, C₁₋₄-alkoxy or halogen. The residue T may be saturated or unsaturated and preferably contains not greater than 18 carbon atoms. Examples of suitable carboxylic acids T-COOH are glycolic, lactic, caproic, lauric, oleic, linoleic, stearic, methoxy acetic, ricinoleic, 12-hydroxy stearic, 12-hydroxy dodecanoic, 5-hydroxy dodecanoic, 5-hydroxy decanoic, 4-hydroxy decanoic, isobutyric, 2-ethylbutyric, isovaleric, 2,2-dimethylbutyric, 2-methylvaleric, 2-propylpentanoic, 2-ethylhexanoic acids and C₁₂₋₂₄-branched chain aliphatic acids available as Isocarbs from Condea.

30 Many of the hydroxycarboxylic acids which are used to prepare the polyester chains are available commercially as mixtures which contain a carboxylic acid which is free from hydroxy groups. The carboxylic acid which is free from hydroxy groups can, thereby, act as the polymerisation terminating group, e.g. commercially available 12-hydroxy stearic acid often contains some stearic acid.

35 As noted hereinbefore the polyester chains may also be attached to the polyamine or polyimine backbone chain via an ethylenically unsaturated group, for example, using a Michaels addition reaction. In this instance the polyester chain may carry a polymerisation terminating group which is attached to either the terminal hydroxy group of the polyester chain or to the carboxylic acid group of the polyester chain. The polymerisation

terminating group can contain the ethylenically unsaturated group or the ethylenically unsaturated group may be attached to the polyester chain via either the free hydroxyl or free carboxylic acid group when the polymerisation terminating group does not contain the ethylenically unsaturated group.

In one preferred aspect of the invention, the polyester containing an ethylenically unsaturated group is of formula 5



wherein

R is hydrogen or C₁₋₄-alkyl;

R¹ is an aliphatic or aromatic residue containing up to 10 carbon atoms which optionally contains a polyether group derivable from propylene oxide and/or ethylene oxide; and

V and m are as defined hereinbefore.

The compounds of formula 5 may be conveniently prepared by reacting an (alk) acrylic acid carrying a terminal hydroxy group with the appropriate hydroxy carboxylic acid or lactone thereof to build the chain residue represented by (CO-V-O)_m. In this instance the (alk) acrylic acid acts as the polymerisation terminating group.

Preferably, R is either hydrogen or methyl.

Examples of suitable (alk) acrylic acids containing a terminal hydroxy group are hydroxy ethyl (meth) acrylic acid, hydroxy propyl (meth) acrylic acid, hydroxy butyl (meth) acrylic acid, polyethyleneglycol mono (meth) acrylate, poly propyleneglycol mono (meth) acrylate, polyethyleneglycol - polypropyleneglycol mono (meth) acrylate, polyethyleneglycol - polytetramethylene glycol mono (meth) acrylate and poly propyleneglycol - polytetramethyleneglycol mono (meth) acrylate (e.g. Blemmer PE, Blemmer PP ex Nihon Yushi Co. Ltd.).

The dispersants according to the present invention may be prepared by any means known to the art. Thus, where the polyesters are attached to the polyamine or polyimine backbone chain via amide and/or salt linkages the polyesters are preferably reacted with the polyamine or polyimine by heating at temperatures between 50°C and 250°C, preferably in an inert atmosphere. Preferably the temperature is not less than 80°C and especially not less than 100°C. In order to minimise charring of the dispersant, the temperature is preferably not greater than 150°C.

The inert atmosphere may be provided by any gas which does not react with the dispersant or the starting materials and includes the inert gases of the Periodic Table and especially nitrogen.

When the dispersant containing amide and/or salt linkages is prepared in a single stage by reacting the polyamine or polyimine with the appropriate polymerisation terminating compound, hydroxycarboxylic acids or lactones thereof it is preferred to include an esterification catalyst such as tetra-alkyl titanate, for example tetra butyl titanate, zinc salt of an organic acid, for example zinc acetate, zirconium salt of an aliphatic alcohol, for example zirconium isopropoxide, aryl sulphonic acid, for example toluene sulphonic acid, or a strong organic acid such as halo acetic acid, for example trifluoroacetic acid. Zirconium isopropoxide is preferred. When the dispersant is prepared by a single stage process, higher temperatures may be required and these are typically from 150°C to 180°C.

As noted hereinbefore it is preferred to prepare the polyester chains or TPOAC acids separately, prior to reacting them with the polyamine or polyimine. In this case, the hydroxycarboxylic acids or lactones thereof and polymerisation terminating compound are reacted together in an inert atmosphere at 150-180°C and preferably in the presence of an esterification catalyst. The subsequent reaction with the polyamine or polyimine may then be carried out at 100-150°C.

Typical conditions for preparing the dispersants containing amide and/or salt linkages are as described in WO 94/21368 and WO 98/19784.

The compounds of formula 5 may be conveniently prepared by reacting the (alk) acylic acid containing a terminal hydroxy group with the relevant hydroxycarboxylic acids or lactones thereof at from 50°C to 150°C, preferably from 80°C to 120°C in the presence of air and oxygen. Preferably the reaction is carried out in the presence of an esterification catalyst such as tetra alkyl titanate, for example tetra butyl titanate, a metal alkoxide such as tetra isopropyl titanate, a tin catalyst such as stannous chloride, stannous octylate or mono butyl tin oxide or an acid catalyst such as p-toluene sulphonic acid or trifluoro acetic acid. The reaction is also preferably carried out in the presence of a polymerisation inhibitor to prevent the self-polymerisation of the (alk) acrylic acid containing the terminal hydroxy group. Examples of suitable inhibitors are (methyl) hydroquinone, phenothiazine and air (oxygen).

The reaction between the polyamine or polyimine and the compound of formula 5 is preferably carried out between 10°C and 130°C, especially between 20°C and 100°C and preferably in an inert solvent. Examples of suitable inert solvents are aromatic and aliphatic solvents such as xylene, toluene and Solvesso, ketones such as acetone, methylethylketone and methylisobutylketone, alkanols such as n-butanol and isopropanol and esters such as dimethyladipate, dimethylsuccinate and dimethylglutarate.

The dispersants according to the invention may also contain polyoxyalkylene carbonyl chains or polyoxyalkenylene carbonyl chains which are attached to the polyamine or polyimine by different linking mechanisms, for example, polyoxyalkylene carbonyl or polyoxyalkenylene carbonyl chains linked to the polyamine or polyimine via

amide and/or salt linkages and polyoxyalkylene carbonyl chains or polyoxyalkenylene carbonyl chains linked to the polyamine or polyimine via an ethylenically unsaturated group.

When The Dispersant contains free amino or imino groups these may be converted into substituted ammonium groups by reaction with an acid or quaternising agent so that The Dispersant is in the form of a substituted ammonium salt. Suitable reagents for this purpose are mineral and strong organic acids or acidic salts such as acetic acid, sulphuric acid, alkyl sulphonic acids, alkyl hydrogen sulphates and aryl sulphonic acids including acid forms of dyestuffs and pigments (i.e. coloured acids) and quaternising agents such as dialkyl sulphates, for example, dimethyl sulphate and alkyl halides, such as methyl and ethyl chloride.

The term 'coloured acid' means an organic pigment or dyestuff containing at least one, preferably from 1 to 6 acid groups, especially sulphonic, phosphoric or carboxylic acid groups. A preferred coloured acid is copper phthalocyanine or other deeply coloured pigment and especially sulphonated copper phthalocyanine containing, on average, from 0.5 to 3 sulphonic acid groups per molecule.

Where the polyester chains are attached to the polyimine or polyamine via amide or salt linkages, useful dispersants have been obtained where POAC 2 is obtainable from poly(12-hydroxy stearic acid) optionally end-capped by stearic acid or poly (ricinoleic acid) optionally end capped by oleic and/or linoleic acid, especially where the number average molecular weight is between 1000 and 2400, for example between 1200 and 2000. Useful dispersants have also been obtained where POAC 2 is obtainable from ricinoleic acid and ϵ -caprolactone in the molar ratio of from 4:1 to 1:4, especially from 2:1 to 1:2 and especially where the number average molecular weight is from 1000 to 2400, for example between 1200 and 2000. These dispersants which have been found particularly useful also contain the residue of a POAC 1 polyester which is either ϵ -caprolactone optionally end-capped with lauric acid or a polyester obtainable from lauric acid, ϵ -caprolactone and δ -valerolactone and which preferably have a number average molecular weight between 1000 and 2400, for example between 1200 and 2000. Dispersants wherein the molar ratio of lauric acid to other lactone(s) is from 1:10 to 1:20 have been found especially useful. Where POAC 1 is derivable from ϵ -caprolactone and δ -valerolactone, dispersants have been found particularly useful which contain a molar ratio of ϵ -caprolactone to δ -valerolactone of from 1:1 to 6:1. In these particularly useful dispersants the molar ratio of POAC 1 to POAC 2 is from 2:1 to 4:1 and the amount of amine/imine groups reacted with POAC 1 and POAC 2 is, together, from 40 to 60%, by weight of the primary and secondary amine groups which are available for reaction with the polyester chains.

As noted hereinbefore, The Dispersant is particularly useful for dispersing a particulate solid in an organic medium which may be either polar or non-polar.

According to a further aspect of the invention there is provided a composition comprising a particulate solid and The Dispersant.

According to a still further aspect of the invention there is provided a dispersion comprising The Dispersant, a particulate solid and an organic medium.

5 The solid present in the dispersion may be any inorganic or organic solid material which is substantially insoluble in the organic medium at the temperature concerned and which it is desired to stabilise in a finely divided form therein.

10 Examples of suitable solids are pigments for solvent inks; pigments, extenders and fillers for paints and plastics materials; dyes, especially disperse dyes; optical brightening agents and textile auxiliaries for solvent dyebaths, inks and other solvent application systems; solids for oil-based and invert-emulsion drilling muds; dirt and solid particles in dry cleaning fluids; particulate ceramic materials; magnetic materials and magnetic recording media, and biocides, agrochemicals and pharmaceuticals which are applied as dispersions in organic media.

15 A preferred solid is a pigment from any of the recognised classes of pigments described, for example, in the Third Edition of the Colour Index (1971) and subsequent revisions of, and supplements thereto, under the chapter headed "Pigments". Examples of inorganic pigments are titanium dioxide, zinc oxide, Prussian blue, cadmium sulphide, iron oxides, vermilion, ultramarine and the chrome pigments, including chromates, 20 molybdates and mixed chromates and sulphates of lead, zinc, barium, calcium and mixtures and modifications thereof which are commercially available as greenish-yellow to red pigments under the names primrose, lemon, middle, orange, scarlet and red chromes. Examples of organic pigments are those from the azo, disazo, condensed azo, thioindigo, indanthrone, isoindanthrone, anthanthrone, anthraquinone, isodibenzanthrone, 25 triphendioxazine, quinacridone and phthalocyanine series, especially copper phthalocyanine and its nuclear halogenated derivatives, and also lakes of acid, basic and mordant dyes. Carbon black, although strictly inorganic, behaves more like an organic pigment in its dispersing properties. Preferred organic pigments are phthalocyanines, especially copper phthalocyanines, monoazos, disazos, indanthrones, anthranthrones, 30 quinacridones and carbon blacks.

35 Other preferred solids are: extenders and fillers such as talc, kaolin, silica, barytes and chalk; particulate ceramic materials such as alumina, silica, zirconia, titania, silicon nitride, boron nitride, silicon carbide, boron carbide, mixed silicon-aluminium nitrides and metal titanates; particulate magnetic materials such as the magnetic oxides of transition metals, especially iron and chromium, e.g. $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , and cobalt-doped iron oxides, calcium oxide, ferrites, especially barium ferrites; and metal particles, especially metallic iron, nickel, cobalt and alloys thereof; and agrochemicals such as the fungicides flutriafen, carbendazim, chlorothalonil and mancozeb.

The organic medium present in the dispersions of the invention is preferably a polar organic medium or a substantially non-polar aliphatic or aromatic hydrocarbon or halogenated hydrocarbon. By the term "polar" in relation to the organic medium is meant an organic liquid or resin capable of forming moderate to strong bonds as described in the article entitled "A Three Dimensional Approach to Solubility" by Crowley et al in Journal of Paint Technology, Vol. 38, 1966, at page 269. Such organic media generally have a hydrogen bonding number of 5 or more as defined in the abovementioned article.

Examples of suitable polar organic liquids are amines, ethers, especially lower alkyl ethers, organic acids, esters, ketones, glycols, alcohols and amides. Numerous specific examples of such moderately strongly hydrogen bonding liquids are given in the book entitled "Compatibility and Solubility" by Ibert Mellan (published in 1968 by Noyes Development Corporation) in Table 2.14 on pages 39-40 and these liquids all fall within the scope of the term polar organic liquid as used herein.

Preferred polar organic liquids are dialkyl ketones, alkyl esters of alkane carboxylic acids and alkanols, especially such liquids containing up to, and including, a total of 6 carbon atoms. As examples of the preferred and especially preferred liquids there may be mentioned dialkyl and cycloalkyl ketones, such as acetone, methyl ethyl ketone, diethyl ketone, di-isopropyl ketone, methyl isobutyl ketone, di-isobutyl ketone, methyl isoamyl ketone, methyl n-amyl ketone and cyclohexanone; alkyl esters such as methyl acetate, ethyl acetate, isopropyl acetate, butyl acetate, ethyl formate, methyl propionate, methoxy propylacetate and ethyl butyrate; glycols and glycol esters and ethers, such as ethylene glycol, 2-ethoxyethanol, 3-methoxypropylpropanol, 3-ethoxypropylpropanol, 2-butoxyethyl acetate, 3-methoxypropyl acetate, 3-ethoxypropyl acetate and 2-ethoxyethyl acetat ; alkanols such as methanol, ethanol, n-propanol, isopropanol, n-butanol and isobutanol and dialkyl and cyclic ethers such as diethyl ether and tetrahydrofuran.

The substantially non-polar, organic liquids which may be used, either alone or in admixture with the aforementioned polar solvents, are aromatic hydrocarbons, such as toluene and xylene, aliphatic hydrocarbons such as heptane, octane and decane, petroleum distillates such as white spirits and halogenated aliphatic and aromatic hydrocarbons, such as trichloro-ethylene, perchloroethylene, chlorobenzene and dichlorobenzene.

Examples of suitable polar resins, as the medium for the dispersion form of the present invention, are film-forming resins such as are suitable for the preparation of inks, paints and chips for use in various applications such as paints and inks. Examples of such resins include polyamides, such as Versamid™ and Wolfamid™, and cellulose ethers, such as ethyl cellulose and ethyl hydroxyethyl cellulose. Examples of paint resins are short, medium and long oil length alkyd resins, alkyd/melamine formaldehyde, alkyd/urea-formaldehyde, alkyd/urea-formaldehyde acid cured, base coat acrylic/cellulose acetate butyrate/melamine-formaldehyde, polyester/melamine-formaldehyde, base coat

polyester/cellulose acetate butyrate/melamine-formaldehyde, base coat nitrocellulose, epoxy, epoxy/amine cured, hydroxy acrylic/isocyanate cured, nitrocellulose and wood stains, polyesters, polyurethane 2-pack, silicone modified polyesters, thermoplastic acrylics, thermo setting acrylics, thermo setting acrylic/melamine-formaldehyde, urethane, vinyl acetate/PVC copolymers and multi media resins such as acrylic and urea aldehyde.

If desired, the dispersions may contain other ingredients, for example resins (where these do not already constitute the organic medium) binders, fluidising agents (such as those described in GB-A-1508576 and GB-A-2108143), anti-sedimentation agents, plasticisers, levelling agents and preservatives.

The dispersions typically contain from 5 to 95% by weight of the solid, the precise quantity depending on the nature of the solid and the quantity depending on the nature of the solid and the relative densities of the solid and the organic medium. For example, a dispersion in which the solid is an organic material, such as an organic pigment, preferably contains from 15 to 60% by weight of the solid whereas a dispersion in which the solid is an inorganic material, such as an inorganic pigment, filler or extender, preferably contains from 40 to 90% by weight of the solid based on the total weight of dispersion.

The dispersion may be obtained by any of the conventional methods known for preparing dispersions. Thus, the solid, the organic medium and The Dispersant may be mixed in any order, the mixture then being subjected to a mechanical treatment to reduce the particles of the solid to an appropriate size, for example by ball milling, bead milling, gravel milling or plastic milling until the dispersion is formed. Alternatively, the solid may be treated to reduce its particle size independently or in admixture with either the organic medium or The Dispersant, the other ingredient or ingredients then being added and the mixture being agitated to provide the dispersion.

If the composition is required in dry form, the liquid medium is preferably volatile so that it may be readily removed from the particulate solid by a simple separation means such as evaporation. It is preferred, however, that the dispersion comprises the liquid medium.

If the dry composition consists essentially of The Dispersant and the particulate solid, it preferably contains at least 0.2%, more preferably at least 0.5% and especially at least 1.0% of The Dispersant based on weight of the particulate solid. Preferably the dry composition contains not greater than 100%, preferably not greater than 50%, more preferably not greater than 20% and especially not greater than 10% by weight based on the weight of the particulate solid.

As described hereinbefore, The Dispersant is particularly suitable for preparing mill-bases where the particulate solid is milled in a liquid medium in the presence of both a particulate solid and a film-forming resin binder.

Thus, according to a still further aspect of the invention there is provided a mill-base comprising a particulate solid, The Dispersant and a film-forming resin.

Typically, the mill-base contains from 20 to 70% by weight particulate solid based on the total weight of the mill-base. Preferably, the particulate solid is not less than 30 and especially not less than 50% by weight of the mill-base.

5 The amount of resin in the mill-base can vary over wide limits but is preferably not less than 10%, and especially not less than 20% by weight of the continuous/liquid phase of the mill-base. Preferably, the amount of resin is not greater than 50% and especially not greater than 40% by weight of the continuous/liquid phase of the mill-base.

The amount of The Dispersant in the mill-base is dependent on the amount of particulate solid but is preferably from 0.5 to 5% by weight of the mill-base.

10 Dispersions and mill bases containing The Dispersant are particularly suitable for use in paints, especially high solids paints, inks, especially flexographic, gravure and screen inks, and non-aqueous ceramic processes, especially tape-coating, doctor-blade, extrusion and injection moulding type processes.

15 The dispersants of the present invention exhibit advantage over similar known dispersants which contain only the one type of polyester chain. In particular, they exhibit superior solubility in organic media such as solvents and do not separate or crystallise when stored at 4°C for lengthy periods. When stored at low temperatures, separation can occur at -24°C but the dispersants readily re-dissolve on warming to 4-10°C. When incorporated into paints and painting inks, The Dispersant gives rise to higher gloss readings and lower haze values in the resultant paints and inks. The Dispersants also exhibit reduced flocculation in multi media tinter paints and inks.

20 The invention is further illustrated by the following examples wherein all references to amounts are in parts by weight unless indicated to the contrary.

25 Example 1

a) Preparation of Polyester 1

Ricinoleic acid (500 parts, 1.68 M ex Fisher) and zirconium-n-butoxide (2.5 parts) were stirred at 170°C under nitrogen until the number average molecular weight was between 1500 and 1800 and the acid value of the polyester was about 35 mg KOH/gm. 30 The water produced in the reaction was removed by means of a Dean-Stark equipment. This is Polyester 1.

b) Preparation of Polyester 2 (LA 1, ϵ -cap 12, δ -val 3)

35 Lauric acid (45 parts, 0.225 M ex Aldrich), ϵ -caprolactone (307.6 parts, 2.7 M ex Aldrich), δ -valerolactone (67.5 parts, 0.675 M ex Aldrich) and zirconium-n-butoxide (10.5 parts) were stirred under nitrogen at 170°C until the number average molecular weight was between 1500 and 1800 and the acid value of the polyester was about 30 mgs KOH/gm. This is Polyester 2.

c) Preparation of Dispersant

Polyester 1 (80 parts) and Polyester 2 (350.2 parts) were stirred under nitrogen at 60°C. Polyethyleneimine (29.59 parts SP200 ex Nippon Shokubai) was added and the reactants stirred at 120°C under nitrogen for 18 hours until the acid value of the dispersant was 20 mg KOH/gm with a base equivalent of 1550. On cooling, the product was obtained as a yellow semi-solid. This is Dispersant 1. The molar ratio of Polyester 1 to Polyester 2 is 1:4 and the polyethyleneimine backbone chain contains polyester chains attached by 35.5% salt linkages and 38.3% amide linkages.

10 Example 2

A millbase was prepared by milling together transparent red iron oxide pigment (49.13 parts, Bayferrox Red 130M ex Bayer), dispersant (1.22 parts), aldehyde/urea film-forming resin (14.87 parts, Laropal A-81 as 60% (w/w) solution in methoxy propyl acetate) and methoxy propyl acetate (4.97 parts). The milling was carried out on a Skandex bead mill for 30 minutes using 3 mm diameter glass beads (125 parts). After removing the glass beads, the above millbase (1 part) was stirred into a white base paint containing titanium dioxide pigment (10 parts).

The white base paint containing the red tinter was coated onto a card using a K-proofer and number 6 K-bar to give a paint film thickness of 60 μ . A drop of the paint formulation was then applied to the paint film and rubbed into the surface using finger pressure until the paint film became tacky. It was then dried at 25°C for 4 hours.

The L, a, b colour co-ordinates were then measured for the rubbed area and also the area of paint film to which no additional paint had been applied. The difference between these two sets of measurements (ΔE) gives a measure of acceptance of the universal tinter (red oxide pigment) by the white base paint.

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

ΔL is $L_1 - L_2$, Δa is $a_1 - a_2$ and Δb is $b_1 - b_2$ where subscript 1 relates to the paint film to which no additional paint was applied and subscript 2 refers to the paint film to which additional paint was applied followed by finger rubbing.

A comparison of the dispersion characteristics for Dispersant 1 and a 50/50 (w/w) mixture of Dispersant A (1:1 molar ratio of ricinoleic acid and ϵ -caprolactone reacted with polyethyleneimine (MW 10,000) in 13:1 (w/w) ratio) and Dispersant B (polyester from lauric acid, ϵ -caprolactone and δ -valerolactone (1:12:3 molar ratio) reacted with polyethyleneimine (MW 10,000) in 13:1 (w/w) ratio) for different white base paints is given in Table 1 below.

These results indicate the universal nature of Dispersant 1.

Table 1

Dispersant 1 Control		White-base paint							
		Epoxy		Air-dried alkyd		Acrylic		Polyurethane	
		Strength	ΔE	Strength	ΔE	Strength	ΔE	Strength	ΔE
		99.31	0.37	97.08	2.74	120.2	0.57	102.3	1.09
		100	1.49	100	2.89	100	3.71	100	1.92

Footnote to Table 1

5 Epoxy base paint is Epilife White ex Marcel Guest.

Air-dried alkyd is ex CIN, Portugal.

Acrylic is Acrythane White ex Marcel Guest.

Polyurethane is Standathane White ex Marcel Guest.

10 Preparation of Polyesters Intermediates (POAC 1)

Example 1(b) was repeated to give the polyester listed in Table 2 below wherein the numerical values indicate the molar ratios of the components.

Table 2

Polyester	Structure of POAC 1
3	lauric:cap (1:12)
4	lauric:cap:val (1:9:4)
5	lauric:cap;glycolic (1:10:3)
6	methoxyacetic:cap:5-Mecap (1:11:2)
7	methoxyacetic:cap:4-Mecap (1:12:2)

Footnote to Table 2.

Lauric is lauric acid

cap is ϵ -caprolactoneval is δ -valerolactone

20 glycolic is glycolic acid

methoxy acetic is methoxyacetic acid

5-Mecap is 5-methyl- ϵ -caprolactone4-Mecap is 4-methyl- ϵ -caprolactone

The preparation of 4-Mecap and 5-Mecap is describe in WO 98/19784.

Preparation of Acrylate (POAC 1) HEA (1), cap (10), val (3)

2-Hydroxyethyl acrylate (33.58 parts, 0.29M ex Aldrich), ϵ -caprolactone (329.9 parts, 2.89M ex Solway Interlox) and δ -valerolactone (86.6 parts, 0.86M ex BASF) were stirred together at 65°C for 72 hours in the presence of methylhydroquinone (0.06 parts ex Aldrich) and tin (II) 2-ethylhexanoate (0.6 parts ex Aldrich) whilst passing air through the reactants. After cooling, the product was obtained as a pale yellow oil. This is Polyester 8.

10

Preparation of Polyester Intermediates (POAC 2)

Preparation of PHS (MW 1600) (POAC 2)

Xylene (348 parts) and 12-hydroxystearic acid (3350 parts having acid and hydroxy values of 182 mg KOH/gm and 160 mg KOH/gm, respectively) were stirred together for 22 hours at 190-200°C in a reactor equipped with a Dean and Stark collector. After 152 parts water had been removed the xylene was removed at 200°C under nitrogen. On cooling, the intermediate was obtained as a pale amber liquid having an acid value of 35 mg KOH/gm. This is Polyester 9.

20

Preparation of SA end-capped PHS (POAC 2)

Polyester 9 (353 parts) and stearic acid (33.62 parts ex Aldrich) were stirred together at 190°C for 18 hours under nitrogen in the presence of zirconium n-butoxide (0.23% w/w ex Aldrich). After cooling, the fully end-capped polyester was obtained as a pale yellow oil having an acid value of 27mg KOH/g. This is Polyester 10.

25

Preparation of cap:ric (5:1) (POAC 2)

Ricinoleic acid (150 parts ex Akzo) and ϵ -caprolactone (286.2 parts ex Solway Interlox) were stirred under nitrogen for 5 hours at 170°C in the presence of zirconium n-butoxide (0.5% by weight). After cooling, the product was obtained as a yellow oil having an acid value of 37 mg KOH/g. This is Polyester 11.

30

Examples 3 to 16 Preparation of Dispersants

Example 1 (c) was repeated to give the dispersants listed in Table 3 below by using the polyesters and polyethyleneimines indicated in the table.

Table 3

Example	Dispersant	POAC 1		POAC 2		Molar ratio of POAC1:POAC2	PEI (Mn)	Amount of PEI	Ratio of Polyester:P EI ($\frac{w}{w}$)
		Polyester	Amount	Polyester	Amount				
3	2	2	350.2	1	80	4:1	10,000	29.59	14.5:1
4	3	2	324	1	100	3:1	10,000	30.4	13.9:1
5	4	2	258.6	1	130	2:1	10,000	109.7	3.5:1
6	5	2	344.4	1	80	4:1	1,200	29.3	14.5:1
7	6	2	346.5	1	80	4:1	5,000	28.8	14.8:1
8	7	2	343.8	1	80	4:1	25,000	28.3	14.9:1
9	8	2	264.7	1	132.4	2:1	10,000	30	13:1
10	*9	3	248.3	1	119.8	2:1	10,000	30.1	12.3:1
11	10	3	248.3	1	119.8	2:1	10,000	30.1	12.3:1
12	11	4	338	9	55	6:1	10,000	23.4	17:1
13	12	5	317.7	9	46.3	9:1	5,000	36.8	10:1
14	13	4	300.9	10	53.2	6:1	5,000	35.3	10:1
15	14	6	135.1	11	39.4	3:1	1,200	30	6:1
16	15	8	54.3	11	212.8	4:1	1,200	-	17:1

Footnote to Table 3

* The preparation of Dispersant 9 was terminated after 3 hours

Example 17 Preparation of Polyester 7/Polyester 11/PAA

Polyester 7 (248 parts) and Polyester 11 (53.4 parts) were stirred under nitrogen at 130°C. Polyallylamine (177.6 parts as a 10% %_w solution in water, Mn 20,000 ex Nitto Boseki) was added dropwise over 4 hours at 130°C and the water removed from the reactants by stirring under a nitrogen stream at 130°C for 16 hours. The product was obtained as a yellow oil wherein the molar ratio of Polyester 7 to Polyester 11 is 4:1 and the weight ratio of Polyester 7 and Polyester 11 to polyallylamine is 17:1. This is Dispersant 16.

Examples 18 to 32

Dispersants 3 to 16 were evaluated in acrylic and polyurethane paints as described in Example 2. The results are given in Table 4 below which clearly show that the dispersants according to the invention exhibit much superior acceptance levels of the universal tinter (ΔE values) compared with dispersants prepared from a single polyester chain or a mixture of such dispersants.

Table 4

		White Base Paint			
		Acrylic		Polyurethane	
Example	Dispersant	Strength	ΔE	Strength	ΔE
18	2	165	1.03	116	1.03
19	3	103	2.71	104	0.63
20	4	158	0.84	87	2.88
21	5	172	1.24	118	1.29
22	6	157	0.83	123	0.78
23	7	147	1.56	121	1.23
24	8	94	1.93	98	2.5
25	9	100	0.72	94	2.36
26	10	90	0.76	91	2.59
27	11	100	0.45	109	1.4
28	12	103	0.65	93	2.54
29	13	105	0.59	96	1.87
30	14	115	0.5	108	0.83
31	15	105	0.9	109	0.82
32	16	108	0.48	104	0.85
Control	A	100	8.35	100	6.23
Control	A/B	138	4.14	108	2.87

Footnote to Table 3

Dispersant A is as described in Example 2. Dispersant A/B is a 50/50 ^w/_w mixture of Dispersant A and Dispersant 3 as described in Example 2.

CLAIMS

1. A dispersant which comprises a polyamine or polyimine backbone chain containing side chains of two or more different types of polyester chain wherein at least one type of polyester chain is derivable from one or more hydroxy carboxylic acids all of which contain a C₁₋₆-alkylene group or lactone thereof and at least one other type of polyester chain derivable from one or more hydroxy carboxylic acids wherein at least one of the hydroxy carboxylic acids contains a C₈₋₃₀-alkylene or C₈₋₃₀-alkenylene chain or lactone thereof, including salts of such dispersants.

2. A dispersant as claimed in claim 1 which contains side chains from two different types of polyester chain.

3. A dispersant as claimed in either claim 1 or claim 2 wherein the polyester chain containing C₁₋₆-alkylene groups is derivable from optionally alkyl substituted ϵ -caprolactone and δ -valerolactone.

4. A dispersant as claimed in any one of claims 1 to 3 wherein the C₈₋₃₀-alkenylene chain is derivable from ricinoleic acid.

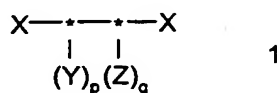
5. A dispersant as claimed in any one of claims 1 to 4 wherein the polyester chains are attached to the polyamine or polyimine backbone via amide and/or salt linkages.

6. A dispersant as claimed in any one of claims 1 to 5 wherein the polyimine is poly (C₂₋₆-alkyleneimine).

7. A dispersant as claimed in claim 6 wherein the polyimine is polyethyleneimine.

8. A dispersant as claimed in any one of claims 1 to 7 wherein the number average molecular weight of the polyamine or polyimine is from 500 to 600,000.

9. A dispersant as claimed in any one of claims 2 to 8 which is represented by formula 1



wherein

X—---X represents the polyamine or polyimine backbone polymer;

Y is the residue of a polyester chain which is derivable from one or more hydroxy carboxylic acids all of which contain a C₁₋₆-alkylene group or lactones thereof;

Z is the residue of a polyester chain which is derivable from one or more hydroxy carboxylic acids at least one of which contains a C₈₋₃₀-alkylene or C₈₋₃₀-alkenylene group or actones thereof;

p and q are integers; and

(p + q) is from 2 to 2000.

10. A dispersant as claimed in claim 9 wherein the molar ratio of p to q is from 1:10 to 10:1.

11. A dispersant as claimed in either claim 9 or claim 10 wherein the molar ratio of p to q is from 1:1 to 5:1.

12. A dispersant as claimed in any one of claims 9 to 11 wherein Y is the residue of a polyester chain derivable from lauric acid, ϵ -caprolactone and δ -valerolactone.

13. A dispersant as claimed in claim 12 wherein the molar ratio of ϵ -caprolactone to δ -valerolactone is from 2:1 to 6:1.

14. A dispersant as claimed in any one of claims 9 to 13 wherein Z is the residue of poly(ricinoleic acid).

15. A composition comprising a particulate solid and a dispersant as claimed in any one of claims 1 to 14.

16. A composition comprising an organic medium and a dispersant as claimed in any one of claims 1 to 14.

17. A dispersion comprising a particulate solid, an organic medium and a dispersant as claimed in any one of claims 1 to 14.

18. A millbase comprising a particulate solid, a film-forming resin, an organic medium and a dispersant as claimed in any one of claims 1 to 14.

19. A paint or printing ink comprising a particulate solid, a film-forming resin, an organic medium and a dispersant as claimed in any one of claims 1 to 14.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01F17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	No relevant documents disclosed	

☐ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.*** Special categories of cited documents :****"A"** document defining the general state of the art which is not considered to be of particular relevance**"E"** earlier document but published on or after the international filing date**"L"** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)**"O"** document referring to an oral disclosure, use, exhibition or other means**"P"** document published prior to the international filing date but later than the priority date claimed**"T"** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention**"X"** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone**"Y"** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.**"&"** document member of the same patent family

Date of the actual completion of the international search

9 November 2000

Date of mailing of the international search report

16/11/2000

Name and mailing address of the ISA

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PATENT COOPERATION TREATY

P. 010MF

File

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:

AVECIA LIMITED
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UNITED KINGDOM

Date of mailing
(day/month/year)

16/11/2000

Applicant's or agent's file reference

SMC/60383/WO

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/GB 00/03335

International filing date
(day/month/year)

31/08/2000

Applicant

AVECIA LIMITED et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

DATE	INITIALS
17/11/00	GT

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.


4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority

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Authorized officer

Gennaro Cappiello

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers;
claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SMC 60383/W0	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 00/ 03335	International filing date (day/month/year) 31/08/2000	(Earliest) Priority Date (day/month/year) 18/09/1999
Applicant AVECIA LIMITED et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01F17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
IPC 7 B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	No relevant documents disclosed -----	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

9 November 2000

Date of mailing of the international search report

16/11/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Fouquier, J-P

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty

For receiving Office use only

International Application No

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) SMC 60383/WO

Box No I TITLE OF INVENTION

Polyester Dispersants

Box No II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below

Avecia Limited
Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is also inventor

Telephone No

0161 740 1460

Facsimile No

0161 721 5801

Teleprinter No

State (that is, country) of nationality:

GB

State (that is, country) of residence:

GB

This person is applicant for the purposes of:

all designated States

☒ all designated States except the United States of America

the United States of America only

the States indicated in the Supplemental Box

Box No III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below

THETFORD, Dean
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is:

applicant only

☒ applicant and inventor

inventor only (If this check-box is marked, do not fill in below)

State (that is, country) of nationality:

GB

State (that is, country) of residence:

GB

This person is applicant for the purposes of:

all designated States

all designated States except the United States of America

☒ the United States of America only

the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet

Box No IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

agent

common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country

FAWKES, David Melville
Intellectual Property Group
Avecia Limited
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

Telephone No

0161 721 2038

Facsimile No

0161 721 5801

Teleprinter No

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent

Continuation of Box No III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below

MAXWELL, Ian Donald
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below

SLATER, Lindsay Anne
Earls Road
Grangemouth
Stirlingshire
FK3 8XG
United Kingdom

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation) The address must include postal code and name of country The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☒ **AP** **ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA** **Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP** **European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA** **OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|---|--|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LC Saint Lucia |
| <input checked="" type="checkbox"/> AG Antigua and Barbuda | <input checked="" type="checkbox"/> LK Sri Lanka |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LR Liberia |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LS Lesotho |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MA Morocco |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BZ Belize | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> MZ Mozambique |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CR Costa Rica | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> DM Dominica | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> DZ Algeria | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TZ United Republic of Tanzania |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> ZA South Africa |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> ZW Zimbabwe |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | Check-box reserved for designating States which have become party to the PCT after issuance of this sheet: |
| <input checked="" type="checkbox"/> KR Republic of Korea | <input type="checkbox"/> |
| <input checked="" type="checkbox"/> KZ Kazakhstan | |

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Supplemental Box If the Supplemental Box is not used, this sheet should not be included in the request ☐

1 ☐ If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No ☐☐☐☐ [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) if more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No ☐☐☐☐ " and indicate for each additional person the same type of information as required in Box No ☐☐☐☐ (The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No ☐☐ or in any of the sub-boxes of Box No ☐☐☐☐, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No ☐☐☐☐ " or "Continuation of Box No ☐☐☐☐ " or "Continuation of Boxes No ☐☐☐☐ and No ☐☐☐☐ " (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No ☐☐ or in any of the sub-boxes of Box No ☐☐☐☐, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No ☐☐☐☐ " or "Continuation of Box No ☐☐☐☐ " or "Continuation of Boxes No ☐☐☐☐ and No ☐☐☐☐ " (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) if, in addition to the agent(s) indicated in Box No ☐☐☐☐, there are further agents: in such case, write "Continuation of Box No ☐☐☐☐ " and indicate for each further agent the same type of information as required in Box No ☐☐☐☐;
- (v) if, in Box No ☐☐☐☐, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No ☐☐☐☐, the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No ☐☐☐☐ " and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No ☐☐☐☐☐☐, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No ☐☐☐☐☐☐ " and indicate for each additional earlier application the same type of information as required in Box No ☐☐☐☐☐☐;
- (vii) if, in Box No ☐☐☐☐☐☐, the earlier application is an ARIPO application: in such case, write "Continuation of Box No ☐☐☐☐☐☐ ", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed ☐

2 ☐ If, with regard to the precautionary designation statement contained in Box No ☐☐☐☐, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded ☐

3 ☐ If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below ☐

Continuation of Box IV

LOCKE, Timothy John
MAYALL, John
PUGSLEY, Roger Graham
REVELL, Christopher
SCHMITT, Maja
SHELLER, Alan

All of Intellectual Property Group, Avecia Limited, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, United Kingdom

Box No VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: * regional Office	international application: receiving Office
item (1) 18/09/1999 18 September 1999	9922039.4	GB		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 1

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4(0)(b)(ii)) ☐ See Supplemental Box

Box No VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA)
(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EPO

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

Box No VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 05

description (excluding sequence listing part) : 19

claims : 02

abstract : 01

drawings :

sequence listing part of description :

Total number of sheets : 27

This international application is accompanied by the item(s) marked below:

1 ☒ fee calculation sheet

2 ☐ separate signed power of attorney

3 ☐ copy of general power of attorney; reference number, if any:

4 ☐ statement explaining lack of signature

5 ☐ priority document(s) identified in Box No VI as item(s):

6 ☐ translation of international application into (language):

7 ☐ separate indications concerning deposited microorganism or other biological material

8 ☐ nucleotide and/or amino acid sequence listing in computer readable form

9 ☐ other (specify):

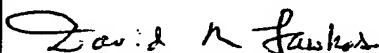
Figure of the drawings which should accompany the abstract:

Language of filing of the international application: ENGLISH

Box No IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request) ☐

For Avecia Limited - D.THETFORD., I.D.MAXWELL and L.A.SLATER



FAWKES, David Melville

For receiving Office use only		2 <input type="checkbox"/> Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
1 <input type="checkbox"/> Date of actual receipt of the purported international application:		
3 <input type="checkbox"/> Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4 <input type="checkbox"/> Date of timely receipt of the required corrections under PCT Article 11(2):		
5 <input type="checkbox"/> International Searching Authority (if two or more are competent): ISA /	6 <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid <input type="checkbox"/>	

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Date of receipt of the record copy by the International Bureau:

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International application No

Date stamp of the receiving Office

Applicant's or agent's
file reference SMC 60383/WO

Applicant
Avecia Limited

CALCULATION OF PRESCRIBED FEES

1 TRANSMITTAL FEE GBP 55 T

2 SEARCH FEE GBP 605 S

International search to be carried out by EPO

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search)

3 INTERNATIONAL FEE

Basic Fee

The international application contains 27 sheets

first 30 sheets GBP 264 b1

remaining sheets x additional amount = b2

Add amounts entered at b1 and b2 and enter total at B GBP 264 B

Designation Fees

The international application contains ALL designations

8 x 56 = GBP 448 D

number of designation fees payable (maximum 8) amount of designation fee

Add amounts entered at B and D and enter total at I GBP 712 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D)

4 FEE FOR PRIORITY DOCUMENT (if applicable) GBP 22 P

5 TOTAL FEES PAYABLE GBP 1394

Add amounts entered at T, S, I and P, and enter total in the TOTAL box TOTAL

The designation fees are not paid at this time

MODE OF PAYMENT

authorization to charge
deposit account (see below)

bank draft

coupons

cheque

cash

other (specify):

postal money order

revenue stamps

DEPOSIT ACCOUNT AUTHORIZATION (this mode of payment may not be available at all receiving Offices)

The RO/ GB is hereby authorized to charge the total fees indicated above to my deposit account

(this check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account

is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account

D02944

30 August 2000

Deposit Account No

Date (day/month/year)

Signature

Kirsty M. Pinder

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

FAWKES, David Melville
AVECIA LIMITED
Intellectual Property Group
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
GRANDE BRETAGNE

NOTIFICATION OF TRANSMITTAL OF
INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

Applicant's or agent's file reference

SMC 60383/WO

IMPORTANT NOTIFICATION

International application No.

PCT/GB 00/03335

International filing date (day/month/year)

31/08/2000

Priority date (day/month/year)

18/09/1999

Applicant

AVECIA LIMITED et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

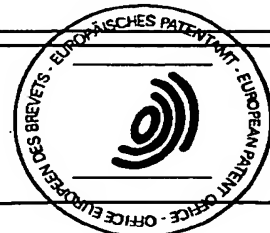
For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 epmu d
Fax: (+49-89) 2399-4465

Authorized officer
Paula Pinazar



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60383/WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB 00/ 03335	International filing date (day/month/year) 31/08/2000	Priority date (day/month/year) 18/09/1999
International Patent Classification (IPC) or national classification and IPC B01F17/00		
Applicant AVECIA LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This **REPORT** consists of a total of 4 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consists of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 12/03/2001	Date of completion of this report 10. 10. 01
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer  H. Senftl



I. Basis of the report

1. This report has been drawn up on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*

☒ the international application as originally filed

☐ the description, pages , as originally filed
pages , filed with the demand
pages , filed with the letter of

☐ the claims, Nos. , as originally filed
Nos. , as amended under Article 19
Nos. , filed with the demand
Nos. , filed with the letter of

☐ the drawings, sheets / fig. , as originally filed
sheets / fig. , filed with the demand
sheets / fig. , filed with the letter of

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.
☐ the drawings, sheets / fig.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2 (c)).

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citation: and explanations supporting such statement

1. Statement

Novelty	Claims	1-19	YES
	Claims		NO
Inventive Step	Claims	1-19	YES
	Claims		NO
Industrial Applicability	Claims	1-19	YES
	Claims		NO

2. Citations and Explanations

Closest prior art are the documents acknowledged on p. 1 of the description. They relate to dispersants having a polyamine or polyimine backbone and pendant polyester chains wherein said chains comprise

- (i) relatively polar oxyalkylenecarbonyl moieties or
- (ii) relatively unpolar oxyalkylenecarbonyl moieties or
- (iii) a random mixture of moieties (i) and (ii).

There is no suggestion in the prior art to have in such dispersants in the same molecule different polyester chains one of which exclusively contains moieties (i) and another of which contains moieties (ii). Consequently, novelty can be acknowledged.

It has been shown in the Examples and Control Examples of the application that the claimed dispersants exhibit considerably better performance than those according to the aforementioned prior art. This is an unexpected technical effect which establishes an inventive step. There is no doubt that the claimed subject-matter is industrially applicable eg for manufacturing paints and inks.

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

1. The ratio 2:1 specified in claim 13 is inconsistent with p. 9, l. 33.
2. Claims 16 and 19 lack clear generic support. Their wording should be included at an appropriate point of the description.
3. For the sake of clarity, the word "molar" should be deleted from claims 10 and 11. The same applies to p. 4, ll. 20-25.
4. It should be explained how formation of lateral polyester chains containing both polar and unpolar moieties can be avoided in the embodiment described on p. 4 , ll. 31-36.
5. The word "ester" should be inserted after "acid" on p. 7, ll. 16 and 20-22 as well as on p. 8, ll. 20+27.
6. Apparently "3" on p. 19, l.3 should be replaced by "B". Likewise "3" on p. 18 l. 11 should read "2".

REC'D 12 OCT 2001

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

14

Applicant's or agent's file reference SMC 60383/WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB 00/ 03335	International filing date (day/month/year) 31/08/2000	Priority date (day/month/year) 18/09/1999
International Patent Classification (IPC) or national classification and IPC B01F17/00		
Applicant AVECIA LIMITED et al.		

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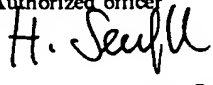
2. This **REPORT** consists of a total of 4 sheets, including this cover sheet.

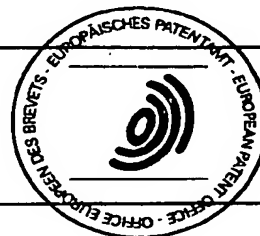
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Date of submission of the demand 12/03/2001	Date of completion of this report 10.10.01
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer  H. Senft



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/GB00/03335

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pages , filed with the demand
pages , filed with the letter of

☐ the claims, Nos. , as originally filed
Nos. , as amended under Article 19
Nos. , filed with the demand
Nos. , filed with the letter of

☐ the drawings, sheets / fig. , as originally filed
sheets / fig. , filed with the demand
sheets / fig. , filed with the letter of

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4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

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	Claims		NO
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	Claims		NO

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